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Computer Simulation of Substituted Polyacetylenes

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) A wide variety of substituted polyacetylenes has been synthesized in recent years (1). Polyacetylene itself is a semiconductor with σ values as high as 10^{-4} Scm^{-1} for oriented films (2); when doped, polyacetylene is a conductor. The conjugated chain has a planar conformation (3). The substituted polymers are primarily insulators, however; the interaction of large substituted groups forces the chain in a non-planar conformation. Poly(1-(trimethylsilyl)-1-propyne), (PTMSP), has been found to be of particular interest, due to its large permeability to gases. The O_2 permeability of PTMSP, for example, is an order of magnitude higher than that of polydimethylsiloxane (1, 4). PTMSP is an amorphous polymer highly soluble in common organic solvents, and is oxidatively stable (5, 6). Values of M_w higher than 10^6 have been achieved (1). Viscosity studies indicate PTMSP has an expanded structure. It is predicted that a given chain's twisted conformation will be maintained even in solution; the barriers for rotation about backbone bonds should prevent a change in conformation. Thus the polymer molecules may be rather rigid, though not rod like. Presumably this rigid, twisted conformation leads to a					
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19. Abstract (concluded)

chain packing of low density, giving rise to the high permeability. In the present studies a series of polyacetylene derivatives have been modelled by quantum mechanics, molecular mechanics, and molecular dynamics techniques to examine the barriers to rotation about backbone bonds and thus the ability to change conformation.

COMPUTER SIMULATION OF SUBSTITUTED POLYACETYLENES

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Introduction:

A wide variety of substituted polyacetylenes has been synthesized in recent years [1]. Polyacetylene itself is a semiconductor with σ values as high as 10^{-4} Scm^{-1} for oriented films [2]; when doped, polyacetylene is a conductor. The conjugated chain has a planar conformation [3]. The substituted polymers are primarily insulators, however; the interaction of large substituted groups forces the chain in a non-planar conformation.

Poly(1-(trimethylsilyl)-1-propyne), (PTMSP), has been found to be of particular interest, due to its large permeability to gases. The O_2 permeability of PTMSP, for example, is an order of magnitude higher than that of polydimethylsiloxane [1, 4]. PTMSP is an amorphous polymer highly soluble in common organic solvents, and is oxidatively stable [5, 6]. Values of M_w higher than 10^6 have been achieved [1].

Viscosity studies indicate PTMSP has an expanded structure. It is predicted that a given chain's twisted conformation will be maintained even in solution; the barriers for rotation about backbone bonds should prevent a change in conformation. Thus the polymer molecules may be rather rigid, though not rod like. Presumably this rigid, twisted conformation leads to a chain packing of low density, giving rise to the high permeability.

In the present studies a series of polyacetylene derivatives have been modelled by quantum mechanics, molecular mechanics, and molecular dynamics techniques to examine the barriers to rotation about backbone bonds and thus the ability to change conformation.

Calculations

Energy-minimized structures were obtained on several repeat units of the polymers in Table I using the MNDO approximation [7] (in the ChemLab II software package on a MicroVAX-II in the Chemistry Department's Molecular Modelling Laboratory). Results for polyacetylene have been previously reported [8]. Barriers to rotation about a C-C single bond were calculated with CNDO/2 [9]. Molecular mechanics and

molecular dynamics calculations were performed using the QUANTA and CHARMM software from the Polygen Corporation on a Stellar GS1000 computer in the Modelling Laboratory.

Results and Discussion

Initially, CNDO/2 calculations were planned to calculate the potential energy as a function of torsion angle about a single C-C bond in the backbone, keeping all other bond lengths and angles fixed. Reasonable results are obtained for trans polyacetylene (PA) as shown in Figure 1. In this figure, 0° represents the trans conformation about the single bond. For substituted polyacetylenes, however, unreasonably high barriers were obtained since the calculations held the remainder of the molecule rigid, as shown in Figure 1 for polypropyne (PP). Thus subsequent studies were made by minimizing energy at each step in the phi scan (molecular mechanics methods), and by obtaining average structures and fluctuations (molecular dynamics).

Some results of dynamics simulations at 300K made on 24 repeat units of the cis structure of the various polyacetylenes are shown in Table I.

Table I. Rotation about backbone bonds in average structures from molecular dynamics simulation at 300K (cis structures).

	Φ (C-C)	Φ (C=C)
Polyacetylene	$\sim 180^\circ$	$\sim 0^\circ$
Poly(2-butyne)	$\sim 28^\circ$ from 180°	$\sim 2^\circ$ from 0°
Poly(tert-butyl acetylene)	$\sim 120-145^\circ$	many close to 0° but several in the range $140-155^\circ$

As the substituted groups increase in size, increasingly large deviations from the planar structure are found. For the poly(tert-butyl acetylene) (PTBA) case, the calculations predict that the large side group force some of the double bond to rotate to large angles form the cis structure.

Energy minimization studies for rotation about single bonds in PTBA have barrier heights on the order 30-40 kcal/mol. Thus the structures can not rapidly change conformation at 300K, and are rigid, though not rod-like. The end-to-end distance for 24 repeat units of PTMSP is shown in Figure 2 for a portion of a dynamics simulation at 300K. Fluctuation about torsional angles allow only small fluctuations in the end-to-end distance. No evidence for rotation over a barrier to a new conformation has been found for PTMSP at reasonable temperatures.

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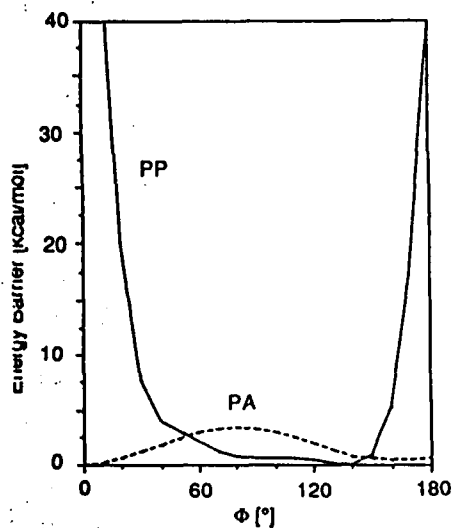


Fig. 1. Energy barriers for rotation about a central single bond for polyacetylene and polypropylene. All other bond lengths, bond angles, and dihedral angles are fixed.

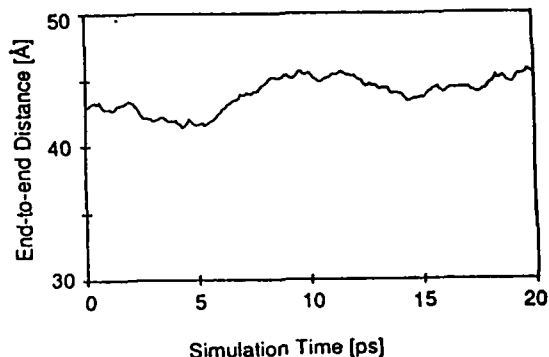


Fig. 2. End-to-end distance for 24 repeat units of PTMSP for part of a molecular dynamics simulation (from 26 to 46 ps) at 300K.



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